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## CLAIMS

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[Claim(s)]

[Claim 1]While the multiple arrays of the discharge cell of one color or a plural color are carried out, a fluorescent substance layer of a color corresponding to each discharge cell is allocated, It is the plasma display device provided with a plasma display panel which the fluorescent substance layer is excited by ultraviolet rays, and emits light, Have said fluorescent substance layer and a green phosphor layer the green phosphor layer, Divalent Eu ion concentration among Eu atoms which constitute a green phosphor at 40% - 95%. A plasma display device, wherein trivalent Eu ion concentration consists of compounds expressed with $Me_{1-x}MgSi_2O_6:Eu_x$ (however, Me, at least one sort in Ca, Sr, and Ba) which is 5% - 60%.

[Claim 2]The plasma display device according to claim 1 characterized by x being 0.2 or less and 0.02 or more in a compound expressed with $Me_{1-x}MgSi_2O_6:Eu_x$ (however, Me, at least one sort in Ca, Sr, and Ba).

[Claim 3]$Me_{1-x}MgSi_2O_6:Eu_x$ which is excited by ultraviolet rays and emits light in visible light (however, Me) A fluorescent substance, wherein it is a fluorescent substance which consists of at least one sort of crystal structures of Ca, Sr, and the Ba(s) and Eu ion concentration trivalent with 40% - 95% in divalent Eu ion concentration is 5% - 60% among Eu atoms which constitute the fluorescent substance.

[Claim 4]The fluorescent substance according to claim 3 characterized by x being 0.2 or less and 0.02 or more in a compound expressed with $Me_{1-x}MgSi_2O_6:Eu_x$ (however, Me, at least one sort in Ca, Sr, and Ba).

[Claim 5]$Me_{1-x}MgSi_2O_6:Eu_x$ which has divalent Eu ion in a parent (however, Me) A manufacturing method of a fluorescent substance calcinating at least one sort of fluorescent substances of Ca, Sr, and the Ba(s) by an oxidizing atmosphere, and making trivalent 5% - 60% of divalent Eu ion.

[Claim 6]$Me_{1-x}MgSi_2O_6:Eu_x$ which has divalent Eu ion in a parent (however, Me) Ca, Sr, and at least one sort of phosphor powder of the Ba(s) in an alcohol solution aluminum, Make it mix and hydrolyze with La, an alkoxide containing an element of Si, or an acetylacetone, and after removing alcohol, it calcinates by an oxidizing atmosphere, A manufacturing method of a fluorescent substance forming aluminum, La, an oxide of Si, or fluoride on the surface of a fluorescent substance making trivalent 5% - 60% of divalent Eu ion.

[Claim 7]$Me_{1-x}MgSi_2O_6:Eu_x$ with divalent Eu ion (however, Me) A manufacturing method of the fluorescent substance according to claim 5, wherein an oxidizing atmosphere of a process of calcinating at least one sort of fluorescent substances of Ca, Sr, and the Ba(s) by an oxidizing atmosphere is oxygen, oxygen-nitrogen, ozone nitrogen, or steam-nitrogen and calcination temperature is 350 ** - 1000 **.

## DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the plasma display device which has a fluorescent substance layer which is used for image display, such as television, and is excited by ultraviolet rays, and emits light.
[0002]
[Description of the Prior Art]In recent years, in the colored presentation device used for image display, such as a computer and television, the plasma display device using a plasma display panel (henceforth PDP) is large-sized, and attracts attention as a colored presentation device which can realize a thin light weight.
[0003]The plasma display device is performing the full color display by carrying out additive color mixing what is called of the three primary colors (red, green, blue). the red (R) who is the three primary colors at a plasma display device in order to perform this full color display, and green -- (G) and blue -- having a fluorescent substance layer which emits light in each color of (B), the fluorescent substance particle which constitutes this fluorescent substance layer is excited by the ultraviolet rays generated within the discharge cell of PDP, and is generating the visible light of each color.
[0004]As a compound used for the fluorescent substance of each above-mentioned color, For example, BO (YGd) $_3$:$Eu^{3+}$ which emits light in red, $Y_2O_3$:$Eu^{3+}$, $Zn_2SiO_4$:$Mn^{2+}$ which emits light in green, and $BaMgAl_{10}O_{17}$:$Eu^{2+}$ which emits light in blue are known. After mixing predetermined raw material, by calcinating at a not less than 1000 ** elevated temperature, solid phase reaction of each of these fluorescent substances is carried out, and they are produced (for example, refer to fluorescent substance handbook P219 and 225 Ohm-Sha). The fluorescent substance particle obtained by this calcination is used after sifting out by grinding (red, green mean-particle-diameter:2micro-5micrometer, blue mean particle diameter: 3micro - 10 micrometers).
[0005]When the reason for grinding a fluorescent substance particle, and sifting out and (classification) carrying out it generally forms a fluorescent substance layer in PDP, the technique of making each color fluorescent substance particle a paste, and screen-stenciling it or the ink jet method make phosphor ink breathe out from a thin nozzle is used.
When a paste is applied, it is easy to acquire the spreading side where the way (particle size distribution has gathered) that the particle diameter of a fluorescent substance is small and uniform is more beautiful.
That is, while a spreading side becomes beautiful and the pack density of the fluorescent substance particle

in a fluorescent substance layer improves so that the particle diameter of a fluorescent substance is small, it is uniform and shape is spherically near, the emission surface area of particles increases and the instability at the time of an address drive is also improved. It is because it is thought that the luminosity of a plasma display device can be raised theoretically.

[0006]

[Problem(s) to be Solved by the Invention]However, the surface area of a fluorescent substance increases by making the particle diameter of a fluorescent substance particle small, or the defect in a fluorescent substance increases. Therefore, the organic matter of much water, carbon dioxide, or a hydrocarbon system adheres to the fluorescent substance surface easily. Especially when divalent Eu ion like $Ba_{1-x}MgAl_{10}O_{17}:Eu_x$ or $CaMgSi_2O_6:Eu$ is a green phosphor used as a luminescence center, Since trivalent Eu which is originally stability is returned to divalent, it has an oxygen deficiency made during a crystal at the time of reduction. If the amount of substitution of Eu increases especially, it has the technical problem that the amount of defects increases (for example, applied physics and volume [ 70th ] No. 3 2001 pp310). For this reason, water and hydrocarbon which exist in the air will stick to the oxygen deficiency Ca under fluorescent substance crystal, Sr, Ba, and near the Eu ion selectively. Therefore, water and hydrocarbon are emitted in a panel in large quantities in a panel production process, and technical problems, such as brightness degradation, a chromaticity variation (the color gap by a chromaticity variation and a screen should be printed), or a fall of a drive margin and a rise of discharge voltage, occur [ be / it / under / discharge / reaction ] with a fluorescent substance and MgO.

[0007]Since ethyl cellulose in a binder becomes difficult to stick to a green phosphor when producing a paste and ink, in order that water and hydrocarbon system gas may stick to a green phosphor selectively, it becomes easy to separate a fluorescent substance and ethyl cellulose. If ethyl cellulose and a fluorescent substance dissociate, when applying phosphor ink from a thin nozzle, a fluorescent substance is deposited near the nozzle orifice part a velocity gradient serves as zero, and the technical problem that blinding of a nozzle is caused as a result generates it.

[0008]In order to solve these technical problems, the method of coating the fluorescent substance surface with the crystal of $aluminum_2O_3$ for the purpose of the defect of these restoring conventionally on the whole surface is devised (for example, JP,2001-55567,A). However, by carrying out a coat to the whole surface, absorption of ultraviolet rays took place and the technical problem that the light emitting luminance of a fluorescent substance falls, and a technical problem called the fall of luminosity according to ultraviolet rays in addition even if it coats occurred.

[0009]This invention was made in view of such a technical problem, is losing the defect of oxygen Ca of a green phosphor, Sr, Ba, and near the Eu ion, and suppresses adsorption of the water on the surface of a green phosphor and hydrocarbon, and an object of this invention is to make an improvement of the brightness degradation and the chromaticity variation of a fluorescent substance, or a discharge characteristic.

[0010]

[Means for Solving the Problem]In order to solve this technical problem, divalent Eu ion concentration is 40% - 95% among Eu atoms in which this invention constitutes a green phosphor, Trivalent Eu ion concentration constitutes a fluorescent substance layer from a compound expressed with $Me_{1-}$

${}_xMgSi_2O_6:Eu_x$ (however, Me, at least one sort in Ca, Sr, and Ba) which is 5% - 60%.

[0011]

[Embodiment of the Invention]By the way, although the fluorescent substance used for PDP etc. is produced with a solid reaction method, solution reaction method, etc., if particle diameter becomes small, it will become easy to generate a defect. In particular, it is known for calcinating a fluorescent substance by reducing atmosphere, or grinding in solid phase reaction that many defects will generate. It is also known also by the ultraviolet rays whose wavelength produced by discharge when driving a panel is 147 nm that a defect occurs in a fluorescent substance (for example, 27th on the Institute of Electronics, Information and Communication Engineers technical research report, EID99-94 January 27, 2000).

[0012]In particular, it is also known that, as for a luminescence ion green phosphor ($BaMgAl_{10}O_{17}:Eu$, $CaMgSi_2O_6:Eu$), divalent Eu has an oxygen deficiency in the fluorescent substance itself (for example, applied physics and volume [ 70th ] No. 3 2001 PP310).

[0013]It has been supposed that it is it the cause of brightness degradation that these defects occur about the conventional green phosphor itself. That is, it has been supposed that it is the cause of degradation the defect made by the shock to the fluorescent substance by the ion by which it is generated at the time of a panel drive, and the defect made by ultraviolet rays with a wavelength of 147 nm.

[0014]As for this invention, the essence of the cause of brightness degradation does not happen only in a defect existing, It found out that water, carbon dioxide, or hydrocarbon system gas sticks to oxygen (O) defect Ca, Sr, Ba, and near the Eu ion selectively, a fluorescent substance reacts to water or hydrocarbon when ultraviolet rays and ion are irradiated by the state where it adsorbed, and brightness degradation and a color gap took place. That is, the knowledge that various degradation took place was acquired by adsorbing water, carbon dioxide, or hydrocarbon system gas at the oxygen deficiency Ca in a green phosphor, Sr, Ba, and near the Eu ion.

[0015]Ethyl cellulose in the binder with which water, carbon dioxide, or hydrocarbon gas sticks to a green phosphor selectively at these defects becomes difficult to stick to a fluorescent substance. Therefore, when fluorescent substances formed a fluorescent substance layer by the ink jet method which stops combining with each other via ethyl cellulose, and applies phosphor ink from a thin nozzle, the knowledge of a fluorescent substance particle having accumulated near [ where a velocity gradient serves as zero ] the nozzle orifice part, and causing blinding was also acquired.

[0016]This invention is reducing the oxygen deficiency in a green phosphor based on these knowledge, and it prevents blinding of a panel making process, the deterioration prevention of the green phosphor at the time of the drive of a panel, and a nozzle, without reducing the luminosity of a green phosphor. Namely, in order to reduce the oxygen deficiency Me of $MeMgSi_2O_6:Eu$, Mg, and near the Eu ion, $MeMgSi_2O_6:Eu$ (however, Me) The oxygen deficiency of a green phosphor is reduced in replacing some divalent Eu ion replaced by Ca in Ca, Sr, and the green phosphor that has at least one sort of crystal structures of the Ba(s), Sr, and Ba ion with trivalent Eu ion.

[0017]Eu (europium) in $MeMgSi_2O_6:Eu$ which is a green phosphor, . If oxidation of a fluorescent substance, etc. replace the part of the divalent ion which goes into the lattice of Me=Ca (calcium), Sr (strontium), or Ba (barium), and exists as a divalent positive ion with trivalent Eu ion, the electric charge of plus will increase

during a crystal. In order that the oxygen which has - electric charge for the oxygen deficiency near Ca, Sr, Ba, and the Eu ion in order to neutralize this + electric charge (in order to compensate an electric charge) may bury, it is thought that the oxygen deficiency as a result can be reduced.

[0018]The more there are few oxygen deficiencies, the more the degree of degradation at each process decreases. However, if trivalent ion increases in number too much, since luminosity will fall, especially the desirable quantity of a trivalent quantity of Eu is 5% - 60% undesirably.

[0019]As a manufacturing method of the fluorescent substance of this invention, it is flux (it $CaF-_2$ and) about a conventional oxide, carbonation thing, or nitric acid ghost raw material. The solid-phase-sintering method, the organic metal salt, and the nitrate using $MgF_2$, $EuF_3$, etc. are used, Although these are hydrolyzed in solution, or the precursor of a fluorescent substance is produced using the coprecipitation method which adds alkali etc. and settles them and the manufacturing method of fluorescent substances, such as a liquid phase process which heat-treats this next, or a fluid atomizing process which is sprayed into the furnace which had the solution containing a fluorescent substance raw material heated, and is produced, can be considered, Even if it used the fluorescent substance produced by which method, it became clear that there was an effect of replacing the part with trivalent ion about the divalent ion of Eu in $MeMgSi_2O_6$:Eu.

[0020]Here, the process by the solid reaction method of a green phosphor is described as an example of the manufacturing method of a fluorescent substance. As a raw material, carbonation things and oxides, such as $CaCO_3$, $SrCO_3$, $BaCO_3$, $MgCO_3$, $SiO_2$, and $Eu_2O_3$, Necessity is accepted and he is Flach (it $CaF-_3$, $EuF-_3$ and) as a sintering accelerator. Add a little $BaCl_2$ and in 2-hour hydrogen-nitrogen ($H_2$-$N_2$) at 1000 ** - 1400 ** After calcination (at this time, all Eu is divalent), Grinding and sieving are performed for this, then, this fluorescent substance is calcinated at 350 ** - 1000 ** according to the oxidizing atmosphere in oxygen ($O_2$), oxygen-nitrogen ($N_2$), steam-nitrogen, or ozone ($O_3$)-nitrogen, and it makes Eu divalent [ a part of ] trivalent. However, the calcination by an oxidizing atmosphere may be oxidized at the same furnace after the reducing process in 1000 ** - 1400 ** between 1000 ** - 350 ** at the time of a temperature fall.

[0021]In the case of the liquid phase process which produces a fluorescent substance from solution, The organic metal salt containing the element which constitutes a fluorescent substance (for example, an alkoxide and an acetylacetone), Or hydrolyze and a coprecipitate (hydrate) is produced, after dissolving a nitrate in water, The granular material produced by spraying it all over calcination or a high temperature furnace in hydrothermal synthesis (it crystallizes in autoclave) and the air is calcinated according to a reducing atmosphere (inside of $H_2$5% and $N_2$) at 1000 ** - 1400 ** for 2 hours, and it sifts out with grinding. Next, this is calcinated at 350 ** - 1000 ** in $O_2$, $O_2$-$N_2$, and $O_3$-$N_2$, and it is considered as a fluorescent substance.

[0022]5% - 60% of an Eu trivalent quantity to Eu divalent is desirable. There are few effects that the amount of substitution prevents blinding and brightness degradation of a nozzle at 5% or less, and since the fall of the luminosity of a fluorescent substance will be seen if it becomes not less than 60%, it is not desirable. About some aforementioned divalent Eu ion having become trivalent, it identified by measurement of EXAFS (X-ray absorption nearedge structure).

[0023]Thus, the conventional green phosphor powder making process is used, and it is $MeMgSi_2O_6$:Eu (however, Me). The divalent ion of Eu under any one or more sort crystal in replacing a part with the trivalent ion of Eu among Ca, Sr, and Ba. A strong (it has endurance in a phosphor baking process, a panel sealing step and the panel aging process, or water and carbon dioxide emitted during a panel drive) green phosphor is obtained to water or hydrocarbon, without reducing the luminosity of a green phosphor. Even if it applies a fluorescent substance layer by the ink jet method, blinding of a nozzle does not take place.

[0024]Namely, the plasma display device concerning this invention, While the multiple arrays of the discharge cell of one color or a plural color are carried out, the fluorescent substance layer of the color corresponding to each discharge cell is allocated, It is the plasma display device provided with the plasma display panel which the fluorescent substance layer is excited by ultraviolet rays, and emits light, Said fluorescent substance layer has a green phosphor layer, and the green phosphor layer comprises green phosphor particles which used 5% - 60% of divalent Eu ion under $MeMgSi_2O_6$:Eu crystal as trivalent Eu ion.

[0025]The green phosphor particles which used 5% - 60% of Eu ion of $MeMgSi_2O_6$:Eu (however, Me, at least one sort in Ca, Sr, and Ba) as trivalent Eu ion have particle diameter as small as 0.05 micrometer - 3 micrometers, and their particle size distribution is also good. If the shape of the fluorescent substance particle which forms a fluorescent substance layer is spherical, pack density will improve further and the emission area of the fluorescent substance particle which contributes to luminescence substantially will increase. Therefore, while the luminosity of a plasma display device also improves, the plasma display device where brightness degradation and a color gap were controlled and which was excellent in luminance property can be obtained.

[0026]Here, the mean particle diameter of a fluorescent substance particle has the still more preferred range of 0.1 micrometer - 2.0 micrometers. The minimum of a maximum droplet size is [ particle size distribution / 1/4 or more / of average value ] still more preferred at 4 or less times of average value. The field at which ultraviolet rays arrive in a fluorescent substance particle is as shallow as about hundreds of nm from a particle surface, and it is in the state where only the surface almost emits light, and if the particle diameter of such a fluorescent substance particle is set to 2.0 micrometers or less, the surface area of the particles which contribute to luminescence will increase, and the luminous efficiency of a fluorescent substance layer will be maintained at a high state. Not less than 20 micrometers of thickness of a fluorescent substance are needed in it being not less than 3.0 micrometers, and discharge space cannot secure enough. Luminosity does not improve that it is it easy to produce a defect to be 0.1 micrometer or less.

[0027]Since discharge space is fully securable, maintaining the state where the luminous efficiency of a fluorescent substance layer is high if thickness of a fluorescent substance layer is carried out within the limits of eight to 25 times of the mean particle diameter of a fluorescent substance particle, luminosity in a plasma display device can be made high. The effect is large in especially the mean particle diameter of a fluorescent substance being 3 micrometers or less (Institute of Image Information and Television Engineers IDY2000-317.PP32).

[0028]As a concrete fluorescent substance particle used for the green phosphor layer in a plasma display device here, The compound expressed with $Me_{1-x}MgSi_2O_6:Eu_x$ (however, Me, at least one sort in Ca, Sr, and Ba) set to 5% - 60% trivalent Eu among divalent Eu ion can be used. Here, its luminosity is highly preferred if the value of X in said compound is 0.02<=X<=0.20. Although each element independent or

mixing may be sufficient as the combination of Ca, Sr, and Ba, it is good. [ of especially the combination of Ca, Sr, Ca, and Ba ]
[0029]As a concrete fluorescent substance particle used for the red phosphor layer in a plasma display device, the compound expressed with $Y_{2X}O_3$:$Eu_X$ or (Y, Gd) $_{1-X}BO_3$:$Eu_X$ can be used. Here, if the value of X in the compound of a red fluorescent substance is 0.05<=X<=0.20, it excels in luminosity and brightness degradation, and it is preferred.
[0030]As a concrete fluorescent substance particle used for the green phosphor layer in a plasma display device, The compound expressed with $Ba_{1-X}$aluminum$_{12}O_{19}$:$Mn_X$ or $Zn_{2-X}SiO_4$:$Mn_X$ can be used. Here, since it is excellent in luminosity and brightness degradation that it is 0.01<=X<=0.10, the value of X in the compound of the above-mentioned green phosphor has it. [ preferred ]
[0031]The manufacturing method of PDP concerning this invention is $MeMgSi_2O_6$:Eu (however, Me) on the substrate of a back panel. The green phosphor particles, red fluorescent substance particles, and green phosphor particles which used as trivalent Eu ion 5% - 60% of Ca, Sr, and divalent Eu of the green phosphor which consists of at least one sort in Ba, The disposing process which applies and allocates from a nozzle the paste which consists of binders, The baking process which makes the binder contained in the paste allocated on the panel burned down, It has the process of piling up and sealing the back panel where the fluorescent substance particle was allocated by the baking process on the substrate, and the front panel in which the display electrode was formed, and luminosity and the plasma display device excellent in brightness degradation can be obtained.
[0032]The fluorescent lamp concerning this invention is a fluorescent lamp which has a fluorescent substance layer which is excited by ultraviolet rays and emits light in visible light, and is $MeMgSi_2O_6$:Eu (however, Me). It can be considered as the fluorescent lamp which the fluorescent substance particle itself excelled [ fluorescent lamp ] in the luminescent characteristic, and was excellent in luminosity and brightness degradation by considering 5% - 60% of Ca, Sr, and divalent Eu of the green phosphor which consists of at least one sort in Ba as the composition set to trivalent Eu.
[0033]Hereafter, the plasma display device by the 1 embodiment of this invention is explained, referring to drawings.
[0034]Drawing 1 is the outline top view which removed the front glass board in PDP, and drawing 2 is a perspective view showing a part about the image display region of PDP in a section. In order to make it intelligible about the number of a display electrode group, a display scan electrode group, and an address electrode group in drawing 1, a part is omitted and it is illustrating.
[0035]As shown in drawing 1, PDP100 The front glass board 101 (not shown), The rear glass substrate 102, the display electrode 103 of N book, and the display scan electrode 104 (the number is attached when N flat knot is shown) of N book, The address electrode group 107 (the number is attached when M flat knot is shown) of M book, It consists of the hermetic-seal layer 121 shown with a slash, and has an electrode matrix of 3 electrode structures by each electrodes 103, 104, and 107, and the cell is formed in the intersection of the display electrode 103 and the display scan electrode 104, and the address electrode 107. 123 is an image display region.
[0036]The front panel in which the display electrode 103, the display scan electrode 104, the dielectric glass layer 105, and the MgO protective layer 106 were allocated on 1 principal surface of the front glass board

101 as this PDP100 was shown in drawing 2, On 1 principal surface of the rear glass substrate 102, the address electrode 107, the dielectric glass layer 108, the septum 109, and the fluorescent substance layer 110R, It has the composition that discharge gas was enclosed in the discharge space 122 which the back panel in which 110G and 110B were allocated is stretched, and is formed between the front panel and a back panel, and the plasma display device is constituted by connecting with the PDP drive shown in drawing 3.

[0037]The plasma display device has the display driver circuit 153, the display scan driver circuit 154, and the address driver circuit 155 in PDP100, as shown in drawing 3, By impressing voltage to the display scan electrode 104 and the address electrode 107 in the cell which you are going to make it turn on according to control of the controller 152, address discharge is performed by the meantime, pulse voltage is impressed between the display electrode 103 and the display scan electrode 104 after that, and maintenance discharge is performed. By this maintenance discharge, ultraviolet rays occur in the cell concerned, a cell lights up because the fluorescent substance layer excited by these ultraviolet rays emits light, and a picture is displayed by the combination of lighting of each color cell, and astigmatism light.

[0038]Next, the manufacturing method is explained about PDP mentioned above, referring to drawing 4 and drawing 5.

[0039]After the front panel first forms the N display electrodes 103 each and the display scan electrode 104 (it is accepting two each and is displaying in drawing 2) alternation and in parallel on the front glass board 101 at stripe shape, It covers with the dielectric glass layer 105 from moreover, and is produced by forming the MgO protective layer 106 on the surface of a dielectric glass layer further.

[0040]The display electrode 103 and the display scan electrode 104 are electrodes which comprise a bus electrode which consists of a transparent electrode which consists of ITO(s), and silver, and the silver paste for bus electrodes is formed by calcinating, after applying by screen-stencil.

[0041]After applying the paste containing the glass material of a lead system by screen-stencil, the dielectric glass layer 105 is formed prescribed temperature and by carrying out predetermined time (it is 20 minutes at 560 **) calcination so that it may become the thickness (about 20 micrometers) of a predetermined layer. As a paste containing the glass material of the above-mentioned lead system, For example, the mixture of PbO (70wt%), $B_2O_3$ (15wt%), $SiO_2$ (10wt%), and aluminum$_2O_3$ (5wt%) and an organic binder (what dissolved 10% of ethyl cellulose in alpha-terpineol) is used. Here, with an organic binder, resin is dissolved in an organic solvent, in addition to ethyl cellulose, an acrylic resin can be used as resin and a butyl kaavie toll etc. can be used as an organic solvent. A dispersing agent (for example, GURISERUTORI oleate) may be made to mix in such an organic binder.

[0042]The MgO protective layer 106 is formed so that it may consist of magnesium oxide (MgO) and a layer may serve as predetermined thickness (about 0.5 micrometer) with sputtering process or a CVD method (chemical vapor deposition).

[0043]On the other hand, a back panel is formed in the state where the address electrodes 107 of M book were installed successively, by forming the silver paste for electrodes by screen printing or the photography method, and calcinating it after that on the rear glass substrate 102, first. The paste which includes the glass material of a lead system on it is applied with screen printing, the dielectric glass layer 108 is formed, and the septum 109 is formed by calcinating, after repeating the paste which similarly includes the glass material of a lead system in a predetermined pitch with screen printing and applying it. By this septum 109, the

discharge space 122 is divided by every one cell (unit luminous region) in a line direction.
[0044]Drawing 4 is a partial sectional view of PDP100. As shown in drawing 4, the gap size W of the septum 109 is specified to 130 micrometers in all - about 240 micrometers at HD-TV which is the constant value of 32 inches - 50 inches. Into the slot between the septa 109, and the inside of divalent Eu ion of red (R) green (G) and $Me_{1-x}MgSi_2O_6:Eu_x$, When 5% - 60% apply the paste state phosphor ink which consists of each fluorescent substance particle and organic binder of blue (B) replaced with trivalent Eu ion, calcinates this at the temperature of 400-590 ** and makes an organic binder burned down, The fluorescent substance layers 110R, 110G, and 110B which each fluorescent substance particle binds are formed. As for thickness L of the laminating direction on the address electrode 107 of these fluorescent substance layers 110R, 110G, and 110B, it is desirable to form in about about 8 to 25 times of the mean particle diameter of each color fluorescent substance particle. That is, in order to absorb without a fluorescent substance layer making the ultraviolet rays generated in discharge space penetrate in order to secure luminosity (luminous efficiency) when a fluorescent substance layer is irradiated with fixed ultraviolet rays, it is desirable for a fluorescent substance particle to hold at least eight layers of thickness laminated about 20 layers preferably. When the thickness laminated about 20 layers is exceeded, it becomes impossible for most luminous efficiency of a fluorescent substance layer to fully secure the size of the discharge space 122 while carrying out a SACHU rate if it becomes the thickness beyond it. While a fluorescent substance layer packing degree will increase even if it is when a lamination number of stages is the same compared with the case where the particles which are not spherical are used if the particle diameter is small enough and spherical like the fluorescent substance particle obtained by the hydrothermal crystallization method etc., Since the whole surface product of a fluorescent substance particle increases, the fluorescent substance particle surface product which contributes to actual luminescence in a fluorescent substance layer increases, and luminous efficiency increases further. 5% - 60% of the synthesizing method of these fluorescent substance layers 110R, 110G, and 110B and divalent Eu ion used for a green phosphor layer mention later the manufacturing method of the green phosphor particles replaced by trivalent Eu ion.
[0045]Thus, the front panel and the back panel which were produced, While being piled up so that each electrode of the front panel and the address electrode of a back panel may intersect perpendicularly, it is sealed by arranging the glass for sealing to a panel edge part, calcinating this to it for 10 to 20 minutes at about 450 **, and making the hermetic-seal layer 121 (drawing 1) form in it. And once exhausting the inside of the discharge space 122 to a high vacuum (for example, $1.1\times10^{-4}$Pa), PDP100 is produced by enclosing discharge gas (for example, inactive gas of a helium-Xe system and a Ne-Xe system) by a predetermined pressure.
[0046]Drawing 5 is an outline lineblock diagram of the ink coater used when forming a fluorescent substance layer. As shown in drawing 5, the ink coater 200 is provided with the server 210, the booster pump 220, the header 230, etc., and the phosphor ink supplied from the server 210 which stores phosphor ink is pressurized by the header 230 with the booster pump 220, and is supplied. The phosphor ink which the ink chamber 230a and the nozzle 240 (inside diameters are micrometers [ 30 ] - 120 micrometers) are formed in the header 230, was pressurized, and was supplied to the ink chamber 230a is continuously breathed out from the nozzle 240. The caliber D of this nozzle 240 is not less than 30 micrometers because of the prevention from blinding of a nozzle, and it is desirable to use below the interval W between the septa 109

(about 130 micrometers - 200 micrometers) for the flash prevention from the septum in the case of spreading, and it is usually set as 30 micrometers - 130 micrometers.

[0047]By carrying out the regurgitation of the phosphor ink 250 continuously from the nozzle 240, while the header 230 is constituted so that it may drive linearly according to the header scanner which is not illustrated, and making the header 230 scan, Phosphor ink is uniformly applied to the slot between the septa 109 on the rear glass substrate 102. Here, the viscosity of the phosphor ink used is maintained at the range of 1500 - 30000CP (centipoise) in 25 **.

[0048]The above-mentioned server 210 is equipped with the agitating equipment which is not illustrated, and precipitate of the particles in phosphor ink is prevented by the stirring. Integral moulding of the header 230 is carried out also including the portions of the ink chamber 230a or the nozzle 240, and a metallic material is produced apparatus processing and by carrying out an electron discharge method.

[0049]As a method of forming a fluorescent substance layer, it is not limited to a described method and various methods, such as the photolitho method, screen printing, and the method of allocating the film which mixed the fluorescent substance particle, can be used, for example.

[0050]Each color fluorescent substance particle, a binder, and a solvent are mixed, phosphor ink is prepared so that it may become 1500 to 30000 centipoise (CP), and it may add a surface-active agent, silica, a dispersing agent (0.1 - 5wt%), etc. if needed.

[0051]As a red fluorescent substance prepared by this phosphor ink, the compound expressed with $_{1-X}$(Y, Gd) $BO_3:Eu_X$ or $Y_{2X}O_3:Eu_X$ is used. These are the compounds in which some Y elements which constitute the parent material were replaced by Eu. Here, as for the amount X of substitution of Eu element to Y element, it is preferred to become the range of 0.05<=X<=0.20. If it is the amount of substitution beyond this, it will be thought that it becomes difficult to use luminosity practically from the brightness degradation of what becomes high becoming remarkable. On the other hand, when it is below this amount of substitution, it is because the composition ratio of Eu which is a luminescence center falls, luminosity falls and it becomes impossible to use it as a fluorescent substance.

[0052]As a green phosphor, the compound expressed with $Ba_{1-X}$aluminum$_{12}O_{19}:Mn_X$ or $Zn_{2-X}SiO_4:Mn_X$ is used. $Ba_{1-X}$aluminum$_{12}O_{19}:Mn_X$, Some Ba elements which constitute the parent material are the compounds replaced by Mn, and $Zn_{2-X}SiO_4:Mn_X$ is the compound in which some elemental Zn which constitute the parent material were replaced by Mn. Here, as for the amount X of substitution of Mn element to a Ba element and elemental Zn, it is preferred to become the range of 0.01<=X<=0.10 for the reason which the above-mentioned red fluorescent substance explained by the way, and the same reason.

[0053]The compound expressed with $Me_{1-x}MgSi_2O_6:Eu_x$ is used as a green phosphor. $Me_{1-x}MgSi_2O_6:Eu_x$ is the compound in which some divalent Me (Me is any one or more sorts of Ca, Sr, and Ba(s)) elements which constitute the parent material were replaced by divalent Eu. Here, as for the amount X of substitution of Eu element to Me element, it is preferred that the former green phosphor serves as the range of 0.02<=X<=0.20 for the same reason as the above. When the amount of substitution of trivalent Eu ion made to replace by said divalent Eu ion is set to $MeEu^{(+2)}{}_{1-a}Eu^{(+3)}{}_{a}MgSi_2O_6:Eu$, it is preferred to become the range of 0.05 <=a<=0.60**. That is, 5% - 60% of range is [ as opposed to / especially / the prevention from blinding of a nozzle ] preferred.

[0054]The synthesizing method of these fluorescent substances is mentioned later.

[0055]alpha-terpineol and a butyl kaavie toll can be used as a solvent, using ethyl cellulose and an acrylic resin as a binder prepared by phosphor ink (0.1 - 10wt% of ink is mixed). Polymers, such as PMA and PVA, can also be used as a binder and organic solvents, such as a diethylene glycol and methyl ether, can also be used as a solvent.

[0056]In this embodiment, what was manufactured by the solid phase calcinating method, the solution method, the spraying calcinating method, and the hydrothermal crystallization method is used for a fluorescent substance particle.

[0057]** a green phosphor ($Me_{1-x}MgSi_2O_6$:$Eu_x$ by a hydrothermal crystallization method) -- in a mixed liquor making process first, Calcium nitrate $Ca(NO_3)_2$, magnesium nitrate $Mg(NO_3)_2$ used as a raw material, Silicon oxide $SiO_2$ and nitric acid europium $Eu(NO_3)_2$ are mixed so that a mole ratio may serve as a chemical formula (however, 0.02<=x<=0.2), this is dissolved in an aquosity medium, and mixed liquor is produced. In that ion exchange water and pure water do not contain an impurity in this aquosity medium, although it is desirable, even if nonaqueous solvents (methanol, ethanol, etc.) are contained in these, it can be used.

[0058]Next, hydration mixed liquor is put into the container which consists of a thing with the corrosion resistance of gold or platinum, and heat resistance, For example, while autoclave etc. pressurize, hydrothermal synthesis (12 to 20 hours) is performed in a high pressure vessel using the device which can be heated under prescribed temperature (100-300 **) and specified pressure (0.2MPa - 10MPa).

[0059]Next, this granular material under reducing atmosphere (for example, atmosphere which contains nitrogen for hydrogen 95% 5%), prescribed temperature -- predetermined time (it is 2 hours at 1000-1400 **) calcination being carried out, and then this being classified, and, By calcinating this at 350 ** - 1000 ** among $O_2$, $O_2$-$N_2$, $H_2O$-$N_2$, or $O_3$-$N_2$, Most Eu of the green phosphor produced under Eu<reducing atmosphere divalent [ in the green phosphor produced under reducing atmosphere ] can obtain green phosphor $Me_{1-x}MgSi_2O_6$:$Eu_x$ of the request which replaced 5% - 60% of divalent> with trivalent Eu. Control of the amount of substitution trivalent from divalent adjusted $O_2$ concentration, oxidation time, and oxidizing temperature.

[0060]$O_2$, $O_2$-$N_2$, $H_2O$-$N_2$, When calcinating in $O_3$-$N_2$, aluminum$_2O_3$ and $SiO_2$, Oxides, such as $La2O_3$, $LaF_2$, $AlF_3$, The organic compound (for example, an alkoxide and an acetylacetone) which contains these elements for the fluoride of ** is used, If a hydrolysis method (how to mix phosphor powder, alcohol, and an organic compound, to hydrolyze an organic compound on the fluorescent substance surface, and to remove and calcinate alcohol after that) is made to use and adhere to the fluorescent substance surface, the deterioration characteristic of a green phosphor and blinding of a nozzle will be improved further. The coating amount of such oxides and fluorides has the necessity that ultraviolet rays pass to desirable necessary minimum. That is, especially 0.01 micrometer or less is desirable 0.1 micrometer or less.

[0061]The fluorescent substance particle obtained by performing hydrothermal synthesis is formed compared with the thing which becomes spherical [ shape ] and by which particle diameter is produced from the conventional solid phase reaction small (mean particle diameter: 0.05 micrometer - about 2.0 micrometers). Although defined as the shaft diameter ratio (a minor axis diameter/major axis diameter) of

almost all fluorescence particles becoming 1.0 or less [ 0.9 or more ] [ here / "spherically" ], for example, not all the fluorescent substance particles necessarily need to go into this range.

[0062]The green phosphor obtained by the atomizing process which sprays this hydration mixture on a high temperature furnace from IZURU, and compounds a fluorescent substance is used without putting said hydration mixture into the container of gold or platinum, It is producible even if it calcinates this in $O_2$, $O_2$-$N_2$, $H_2O$-$N_2$, or $O_3$-$N_2$.

($Me_{1-x}MgSi_2O_6:Eu_x$ by the calcinating-in the air method) This fluorescent substance is produced with a solid reaction method only by $Me_{1-x}MgSi_2O_6:Eu_x$ and the raw material which were mentioned above differing from each other. Hereafter, the raw material to be used is explained.

[0063]As a raw material, calcium hydroxide $Ca(OH)_2$, strontium hydroxide $Sr(OH)_2$, Magnesium hydroxide $Mg(OH)_2$, oxidized silicon $SiO_2$, Weighing of the hydroxylation europium $Eu(OH)_2$ is carried out so that it may become a mole ratio as occasion demands, After mixing these with $EuF_3$ as flux and calcinating this at 1100 ** among the air, prescribed temperature (it is 2 hours at 1100 to 1400 **) calcination is carried out under reducing atmosphere (it is 95% of atmosphere about 5% and nitrogen in hydrogen). Next, $O_2$-$N_2$, $O_2$, $H_2O$-$N_2$, or $O_3$-$N_2$ is introduced into a firing furnace above 1000 ** or less 350 ** under temperature fall (1100 ** - 1400 **), The green phosphor which replaced some divalent ion of Eu with trivalent ion is obtained.

[0064]Although an oxide, a nitrate, and hydroxide were mainly used as a raw material of a fluorescent substance, a fluorescent substance is also producible using the organic metallic compound, for example, a metal alkoxide, containing elements, such as Ca, Ba, Sr, Mg, aluminum, and Eu, a ** acetylacetone, etc. When calcinating in $O_2$, $O_2$-$N_2$, and $O_3$-$N_2$, If aluminum$_2O_3$, $SiO_2$, $AlF_3$, $La_2O_3$, $LaF_2$, etc. are simultaneously coated with the hydrolysis method using a metal alkoxide or an acetylacetone, the deterioration characteristic of a fluorescent substance will be improved further.

[0065]** a green phosphor ($Zn_{2-X}SiO_4:Mn_X$) -- in a mixed liquor making process first, Zinc nitrate Zn $(NO_3)$, nitric acid silicon $Si(NO_3)_2$ which are raw materials, Manganese nitrate $Mn(NO_3)_2$ is mixed so that it may be set to 2-X:1:X (0.01<=X<=0.10) by a mole ratio, after heating this mixed solution at 1500 ** next, impressing an ultrasonic wave from a nozzle, it sprays, and a green phosphor is produced.

($Ba_{1-X}$aluminum$_{12}O_{19}:Mn_X$) First in a mixed liquor making process, Barium nitrate $Ba(NO_3)_2$, aluminium nitrate aluminum$(NO_3)_2$ which are raw materials, It mixes so that manganese nitrate $Mn(NO_3)_2$ may be set to 1-X:12:X (0.01<=X<=0.10) by a mole ratio, and this is dissolved in ion exchange water, and mixed liquor is produced.

[0066]Next, a hydrate is made to form by dropping a basic aqueous solution (for example, aqueous ammonia solution) at this mixed liquor in a hydration process. In a hydrothermal synthesis process, this hydrate and ion exchange water Then, corrosion resistance, such as platinum metallurgy, It puts in the capsule which consists of a thing with heat resistance, for example, predetermined time (for example, 2 to 20 hours) hydrothermal synthesis is performed in a high pressure vessel using autoclave under the conditions of prescribed temperature and specified pressure (for example, the temperature of 100-300 **,

the pressure 0.2M - 10MPa).

[0067]Then, desired $Ba_{1-X}aluminum_{12}O_{19}:Mn_X$ is obtained by drying. By this hydrothermal synthesis process, particle diameter is set to 0.1micro - about 2.0 micrometers, and the fluorescent substance obtained becomes spherical [ that shape ]. Next, this granular material is classified after annealing at 800 ** - 1100 ** in the air, and it is considered as a green fluorescent substance.

[0068]** In a red fluorescent substance (Y, Gd) ($_{1-X}BO_3:Eu_X$) mixed liquor making process, Nitric acid yttrium $Y_2(NO_3)_3$ and water nitric acid GADORIMIUMU $Gd_2(NO_3)_3$ which are raw materials, boric acid $H_3BO_3$, and nitric acid europium $Eu_2(NO_3)_3$ are mixed, After mixing so that a mole ratio may be set to 1-X:2:X (0.05<=X<=0.20) (the ratio of Y to Gd is 65 to 35), and then heat-treating this at 1200 ** - 1350 ** in the air for 2 hours, it classifies and a red fluorescent substance is obtained.

($Y_{2X}O_3:Eu_X$) In a mixed liquor making process, Nitric acid yttrium $Y_2(NO_3)_2$ and nitric acid europium Eu $(NO_3)_2$ which are raw materials are mixed, it dissolves in ion exchange water and mixed liquor is produced so that a mole ratio may serve as 2-X:X (0.05<=X<=0.30).

[0069]Next, a basic aqueous solution (for example, aqueous ammonia solution) is added to this solution, and a hydrate is made to form in a hydration process.

[0070]Then, in a hydrothermal synthesis process, this hydrate and ion exchange water are put in the container which consists of a thing with corrosion resistance, such as platinum metallurgy, and heat resistance, for example, hydrothermal synthesis is performed in a high pressure vessel for 3 to 12 hours using autoclave under the temperature of 100-300 **, the pressure 0.2M - the conditions of 10MPa. Then, desired $Y_{2X}O_3:Eu_X$ is obtained by drying the obtained compound.

[0071]Next, after annealing 1300 ** - 1400 ** of this fluorescent substance in the air for 2 hours, it classifies and is considered as a red fluorescent substance. Particle diameter is set to 0.1micro - about 2.0 micrometers, and the fluorescent substance obtained by this hydrothermal synthesis process becomes spherical [ that shape ]. This particle diameter and shape are suitable for forming the fluorescent substance layer excellent in the luminescent characteristic.

[0072]It is a fluorescent substance conventionally used about the fluorescent substance layers 110R and 110G of PDP100 mentioned above, and the fluorescent substance particle which replaced some Eu divalent ion which constitutes a fluorescent substance with the trivalent ion of Eu was used about the fluorescent substance layer 110B. Since especially the conventional green phosphor has large degradation in each process compared with the green phosphor of this invention, the white color temperature at the time of emitting light simultaneously three color tended to have fallen. Therefore, although the color temperature of a white display is improved in a plasma display device by lowering the luminosity of the cell of fluorescent substances (red, green) other than blue in circuit, If the green phosphor manufactured by the manufacturing method concerning this invention is used, it will become unnecessary for the luminosity of a blue cell to increase, and to lower the luminosity of the cell of other colors intentionally, since there is also little degradation in a panel making process. Therefore, it becomes unnecessary to lower the luminosity of the cell of all the colors intentionally. Therefore, the luminosity of a plasma display device can be raised, maintaining the state where the color temperature of a white display is high, since the luminosity of the cell of all the colors can be used for full.

[0073]The green phosphor concerning this invention is applicable also to the fluorescent lamp which excites and emits light by the same ultraviolet rays. In that case, what is necessary is just to replace divalent Eu ion which constitutes the conventional green phosphor particles applied to the fluorescent tube wall by the fluorescent substance layer which consists of a green phosphor replaced with trivalent Eu ion. Thus, if this invention is applied to a fluorescent lamp, what excelled the conventional fluorescent lamp in luminosity and brightness degradation will be obtained.

[0074]Hereafter, in order to evaluate the performance of the plasma display device of this invention, the sample based on the above-mentioned embodiment was produced, and the quality assessment experiment was conducted on the sample. The experimental result is examined.

[0075]Each produced plasma display device had a size of 42 inches (rib pitch 150micrometer HD-TV specification), and as for the thickness of the dielectric glass layer, the thickness of 20 micrometers and a MgO protective layer produced the distance between 0.5 micrometer, a display electrode, and a display scan electrode so that it might be set to 0.08 mm. The discharge gas enclosed with discharge space is the gas which mixed xenon gas 5% to the subject, and neon is enclosed with predetermined discharge gas pressure.

[0076]Each synthetic condition is shown in Table 1 using the fluorescent substance which replaced divalent Eu ion which constitutes a fluorescent substance with trivalent Eu ion by each green phosphor particle used for the plasma display device of the samples 1-10.

[0077]

[Table 1]

| 試料番号 | 青色蛍光体 [$Me_{1-x}MgSi_2O_6:Eu_x$] | | | | | 赤色蛍光体 [$(Y,Gd)_{1-x}BO_3:Eu_x$] | | 緑色蛍光体 [$(Zn_{1-x}Mn_x)_2SiO_4$] | |
|---|---|---|---|---|---|---|---|---|---|
| | Me及びMeに対するEuの量、x | 製造方法 | 2価のEuを3価のEuにする方法 | Eu2価に対するEu3価の量 | コーティング膜 | Euの量 x | 製造方法 | Mnの量 x | 製造方法 |
| 1 | Ca, x=0.02 | 水熱合成法 | $O_2$中、520℃60分酸化処理 | 5.00% | $Al_2O_3$ | x=0.1 | 固相反応法 | x=0.01 | 噴霧法 |
| 2 | Ca/Sr=1/0.1, x=0.05 | 固相反応法(フラックス法) | $H_2O$-$O_2$中、610℃60分酸化処理 | 15.00% | $SiO_2$ | x=0.2 | 噴霧法 | x=0.02 | 水熱合成法 |
| 3 | Ca/Sr=1/0.1, x=0.1 | 噴霧法 | $N_2$-$O_2$(3%)中、700℃60分酸化処理 | 25.50% | $La_2O_3$ | x=0.3 | 水溶液法 | x=0.05 | 固相反応法 |
| 4 | Ca/Sr/Ba=1/0.1/0.1, x=0.2 | 水溶液法 | $N_2$-$O_2$(30%)中、900℃60分酸化処理 | 55.00% | $LaF_3$ | x=0.15 | 水熱合成法 | x=0.1 | 〃 |
| | 青色蛍光体 [$Me_{1-x}MgSi_2O_6:Eu_x$] | | | | | 赤色蛍光体 [$(Y_{1-x})_2O_3:Eu_x$] | | 緑色蛍光体 [$Ba_{1-x}Al_{12}O_{19}:Mn_x$] | |
| 5 | Ca/Sr=1/1, x=0.2 | 固相反応法(フラックス法) | 降温中1000℃以下で$N_2$-$O_2$(20%)導入し酸化処理 | 60.00% | $SiO_2$ | x=0.01 | 水熱合成法 | x=0.01 | 水熱合成法 |
| 6 | Ca/Sr/Ba=1/1/1, x=0.15 | 水熱合成法 | 降温中900℃以下で$N_2$-$O_2$(20%)導入し酸化処理 | 41.50% | $AlF_3$ | x=0.1 | 噴霧法 | x=0.02 | 噴霧法 |
| 7 | Sr, x=0.15 | 噴霧法 | 降温中750℃以下で$N_2$-$O_2$(1%)導入し酸化処理 | 20.20% | なし | x=0.15 | 水溶液法 | x=0.05 | 固相反応法 |
| 8 | Ba, x=0.05 | 固相反応法 | $H_2O$(0.5%)-$N_2$中、700℃60分酸化処理 | 10.10% | なし | x=0.2 | 固相反応法 | x=0.1 | 〃 |
| 9 | Ca/Sr=1/0.5, x=0.05 | 〃 | $N_2$-(5%)$O_2$中、800℃60分酸化処理 | 20.10% | なし | 〃 | 〃 | 〃 | 〃 |
| 10 | Sr/Ba=1/0.5, x=0.1 | 〃 | $N_2$-(20%)$O_2$中、900℃60分酸化処理 | 36.50% | なし | x=0.15 | 水溶液法 | x=0.01 | 水熱合成法 |
| 11* | Ca, x=0.1, | 固相反応法 | なし | なし | なし | 〃 | 〃 | 〃 | 〃 |

*試料番号11は比較例

[0078]The samples 1-4 to a red fluorescent substance $_{1-X}$(Y, Gd) $BO_3$:$Eu_X$, To a green phosphor, $Zn_{2-X}SiO_4$:$Mn_X$, It is the thing of combination which used $Me_{1-x}MgSi_2O_6$:$Eu_x$ for the green phosphor, Eu and the substitution ratio of Mn used as the method of composition of a fluorescent substance, and a luminescence center, i.e., Y, Me element (however, Me) Trivalent Eu ion content replaced by Ca, Sr, the substitution ratio

of Eu to at least one sort in Ba, the substitution ratio of Mn to elemental Zn, and divalent Eu ion is changed as shown in Table 1. The green phosphor of the samples 1-4 coats an oxide or fluoride with a hydrolysis method using the metal alkoxide containing the element to coat, or an acetylacetone.

[0079]The samples 5-10 to a red fluorescent substance $Y_{2X}O_3$:$Eu_X$, To a green phosphor, $Ba_{1-X}$aluminum$_{12}O_{19}$:$Mn_X$, It is the thing of combination which used $Me_{1-x}MgSi_2O_6$:$Eu_x$ for the green phosphor, Trivalent Eu ion content replaced by divalent Eu ion which constitutes the substitution ratio and green phosphor of the conditions of a fluorescent substance synthesizing method and a luminescence center like the above is changed as shown in Table 1. The samples 5-6 coat an oxide or fluoride with a hydrolysis method.

[0080]The phosphor ink used for formation of a fluorescent substance layer mixed and produced a fluorescent substance, resin, the solvent, and the dispersing agent using each fluorescent substance particle shown in Table 1.

[0081]Viscosity is maintained at the range of 1500 - 30000CP in each result measured about the viscosity (25 **) of the phosphor ink at that time. When the formed fluorescent substance layer was observed, phosphor ink was uniformly applied to the septum wall surface, and, moreover, all have been applied without blinding. About the fluorescent substance particle used for the fluorescent substance layer in each color, the thing of the mean particle diameter of 0.1-3.0 micrometers and the particle diameter of 8 micrometers or less of maximum droplet sizes is used for each sample.

[0082]The sample 11 is a sample using the conventional $CaMgSi_2O_6$:Eu fluorescent substance particle with which processing in particular has not gone to each color fluorescence particle.

[0083]Measurement of Eu ion of Table 1 divalent and trivalent was measured by the XANES method (X-rayabsorption nearedge structure).

[0084](Experiment 1) In a phosphor baking process [ in / which were produced / the samples 1-10 and the comparison sample 11 / a back panel manufacturing process ] (520 **, 20 minutes), The luminosity of each color performed how it would change by the model experiment (the luminosity after spreading and calcination is measured for a paste after calcination of a granular material before the rate of change before and behind calcination of each color, and calcination), and measured luminosity and the rate of a luminance change.

[0085](Experiment 2) The rate of a luminance change (degradation) of each fluorescent substance before and behind the panel lamination process (450 ** of sealing steps, 20 minutes) in a panel production process was measured.

[0086](Experiment 3) measurement of luminosity when a panel is ****ed in each color, and a brightness degradation rate of change follows a plasma display device for 100 hours, impresses a with the voltage 200V and a frequency of 100 kHz maintaining-a-discharge pulse to it, and measures the panel brightness before and behind that -- the brightness degradation rate of change (<) from there [Luminosity before the luminosity-impression after impression] Luminosity >*100 before /impression was calculated.

[0087]It judges by whether a flicker occurs, seeing a picture about the address mistake at the time of address discharge, or there is nothing, and if it is also one place, are and it will **. About the luminance distribution of the panel, the luminosity at the time of a white display was measured with the luminance meter, and distribution of the whole surface was shown. About blinding, continuation spreading was

performed for 200 hours using a nozzle 80 micrometers in inside diameter, and the existence of blinding of a nozzle was investigated.

[0088]The result about the luminosity and the brightness degradation rate of change of each color of these experiments 1-3 is shown in Table 2.

[0089]

[Table 2]

| 試料番号 | 背面パネル工程蛍光体焼成520℃による輝度劣化率（%） | | | パネル張り合せ工程封着時（460℃）における蛍光体の輝度劣化率（%） | | | 200V，100kHz の放電維持パルス100時間印加後のパルスの輝度変化率（%） | | | アドレス放電時のアドレスミス及びノイズの目詰まり（200時間での有無） | 青色全面点燈時の輝度 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 青色 | 赤色 | 緑色 | 青色 | 赤色 | 緑色 | 青色 | 赤色 | 緑色 | | Ｃｄ／ｃｍ² |
| 1 | -0.3 | -1.2 | -4.9 | -0.3 | -2.6 | -13.0 | -0.7 | -4.4 | -14.5 | 共になし | 85.2 |
| 2 | -0.1 | -1.3 | -4.0 | -0.2 | -2.4 | -13.2 | -0.6 | -4.1 | -14.2 | 〃 | 86 |
| 3 | -0.1 | -1.4 | -4.5 | -0.1 | -2.3 | -12.9 | -0.5 | -4.0 | -14.6 | 〃 | 84.1 |
| 4 | 0 | -1.4 | -4.7 | -0.1 | -2.2 | -12.7 | -0.2 | -4.2 | -14.1 | 〃 | 83 |
| 5 | 0.0 | -1.5 | -4.9 | 0.0 | -2.0 | -12.9 | 0.0 | 4.3 | -14.8 | 〃 | 85 |
| 6 | 0.0 | -1.2 | -4.3 | 0.0 | -2.3 | -12.6 | -0.2 | -4.1 | -14.9 | 〃 | 85 |
| 7 | -0.2 | -1.4 | -4.5 | -0.2 | -2.4 | -12.3 | -0.3 | -4.2 | -14.7 | 〃 | 87 |
| 8 | -0.1 | -1.2 | -4.3 | -0.3 | -2.5 | -12.5 | -0.4 | -4.3 | -15.1 | 〃 | 83.5 |
| 9 | -0.2 | -1.5 | -4.1 | -0.2 | -2.1 | -12.8 | -0.5 | -4.1 | -15.6 | 〃 | 84 |
| 10 | 0.0 | -1.3 | -4.2 | -0.2 | -2.3 | -13.0 | -0.2 | -4.1 | -14.8 | 〃 | 85 |
| 11* | -4.6 | -1.3 | -4.2 | -14.5 | -2.3 | -13 | -11 | -4.2 | 14.4 | 共にあり | 61 |

＊試料番号１１は比較例

[0090]As shown in Table 2, in the comparison sample 11, with the sample which has not replaced divalent Eu ion with trivalent Eu ion in a green phosphor. The rate of brightness degradation in each process is large, and especially blue by a phosphor baking process 4.65%, To 11% of brightness lowering being seen by accelerated life testing (200V and 100 kHz) 14.5% by a sealing step, and there being an address mistake and blinding of a nozzle again, about the samples 1-10, all blue rates of change serve as 0.7% or less of value, and, moreover, there is also no address mistake.

[0091]when this replaced 5% - 60% of divalent Eu ion which constitutes a green phosphor with trivalent Eu ion, the oxygen deficiency (especially oxygen deficiency Ca, Sr, Eu, and near the Ba ion) in a green phosphor decreased substantially -- it is a sake. Water and hydrocarbon which came out of the water by a surrounding atmosphere at the time of fluorescent substance calcination, hydrocarbon or MgO at the time of panel sealing and a septum, sealing fritto material, and a fluorescent substance stop for this reason, sticking to the defect layer of the surface of a fluorescent substance.

[0092](Experiment 4) The inside of Eu ion of a green phosphor divalent [ as a model experiment ], After neglecting the fluorescent substance (sample 13) which has not replaced 5% - 60% with trivalent Eu ion for 10 minutes in 60 **90% of relative humidity, It dried at 100 **, and after that, as a result of TDS analysis (temperature-programmed-desorption gas mass spectrometry) of the fluorescent substance of these, as shown in Table 3, more [ 15 times ] results were brought as compared with the sample 12 which the peak of physical adsorption (near 100 **) of water and chemical absorption (300 ** - 500 **) made substitution processing.

[0093]

[Table 3]

| 試料番号 | 蛍光体 | 輝度（cd／m²） | 100V，60Hz 5000時間後の輝度変化 |
|---|---|---|---|
| 12 | 試料番号７の蛍光体 | 6885 | -0.25% |
| 13* | 試料番号１１の蛍光体 | 6600 | -14.6% |

＊試料番号１３は比較例

[0094]
[Effect of the Invention]By replacing 5% - 60% of divalent Eu ion of the green phosphor which constitutes a fluorescent substance layer with trivalent Eu ion as mentioned above according to this invention, Reliability can be raised, while being able to prevent degradation at the various processes of a fluorescent substance layer and being able to improve the luminosity and the life of PDP or a fluorescent lamp.

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[Translation done.]

[Claim 8]A manufacturing method of a fluorescent substance characterized by comprising the following.

A process of mixing an oxide, a carbonation thing, or metal salt containing Ca, Ba, Sr, Mg, Si, and Eu.

A process of calcinating the mixture in the air and decomposing carbonic acid and a salt.

A process of calcinating in reducing atmosphere and making a state of Eu atom divalent.

A process which is calcinated in an oxidizing atmosphere and trivalent makes 5% - 60% at 40% - 95% in divalent [ of Eu ].

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[Translation done.]